Study on the Gas Evolution and Recombination of Sealed Ni/MH Battery

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After a cybernated tiny pressure sensor and a ϕ0.2mm injector needle of chromatogram analyzer had pierced into the air chamber of 1100mAh/g AA-sized Ni/MH battery, the internal gas pressure and composition were *in situ* monitored under different charge/discharge states and at different immersing heights of electrolyte, It's found the internal gas is mainly evolved on the cathode and consequently oxygen is the basic component. When the gas was recombined into water, oxygen diffusion in electrolyte controlled the reaction rate.

As cathode capacity limited structure is adopted in Ni/MH battery, $NiOOH/Ni(OH)_2$ electrode plays an important role in the internal gas cycling. Fig. 1(a) shows the internal gas pressure is going up with changed with the potential of $NiOOH/Ni(OH)_2$ cathode when the battery is in charge. It is clear gas evolution is greatly accelerated at the knee point of cathode potential, indicating it is overcharge of cathode causes oxygen bubbing.

When the battery is discharged or stored, there are two approaches for internal gas to be recombined into water. One is electrochemical process, only happening in discharging. It can be described as:

Cathode: $\frac{1}{2}O_2 + H_2O \rightarrow 2HO^-$

Anode: $yHO^- + MH_x \rightarrow yH_2O + MH_{x-y}$

because there is a step for oxygen gas dissolved into KOH electrolyte, the rate of electrochemical recombination is affected by the oxygen partial pressure and immersing height of electrolyte. Another is chemical process, assumed as oxygen gas reacts with metal hydride directly. Its characteristic is the reaction rate is governed mainly by oxygen partial pressure.

Calculation shows the rate of electrochemical recombination is much more high than that of the chemical process. When we keep oxygen partial pressure at 7atm, corresponding to the cases of half and fully immerged electrodes, the electrochemical recombination rate is 0.45 and 0.15 ml/min. respectively, meanwhile, that of chemical recombination is only 0.04 and 0.02ml/min. at the same cases.

Besides the amount of electrolyte, charge /discharge scheme and electrodes' decay also influence internal gas pressure strongly. Fig. 2 shows at higher current, more gas is accumulated, resulting in a higher maximum pressure. However, the gas annihilation time doesn't show a big difference in Fig. 2 each other, that is the evidence that pressure influences the gas recombination process. As higher pressure arises a faster recombination, the total gas-annihilation time is mainly determined by the reaction rate at lower pressure.

After 200 cycles, the redistribution of electrolyte among the electrodes and separator caused a serious decay upon the battery's performance, especially reduced the discharge capacity and lowered charge efficiency, resulting in an increase of pressure. By recruiting some electrolyte, we recovered battery's discharge capacity to more than 1050mAh, but didn't receive a decrease of pressure. By contrary, it was increased. This result indicates the electrode pore structure is important as well as the amount of electrolyte in internal gas pressure controlling.

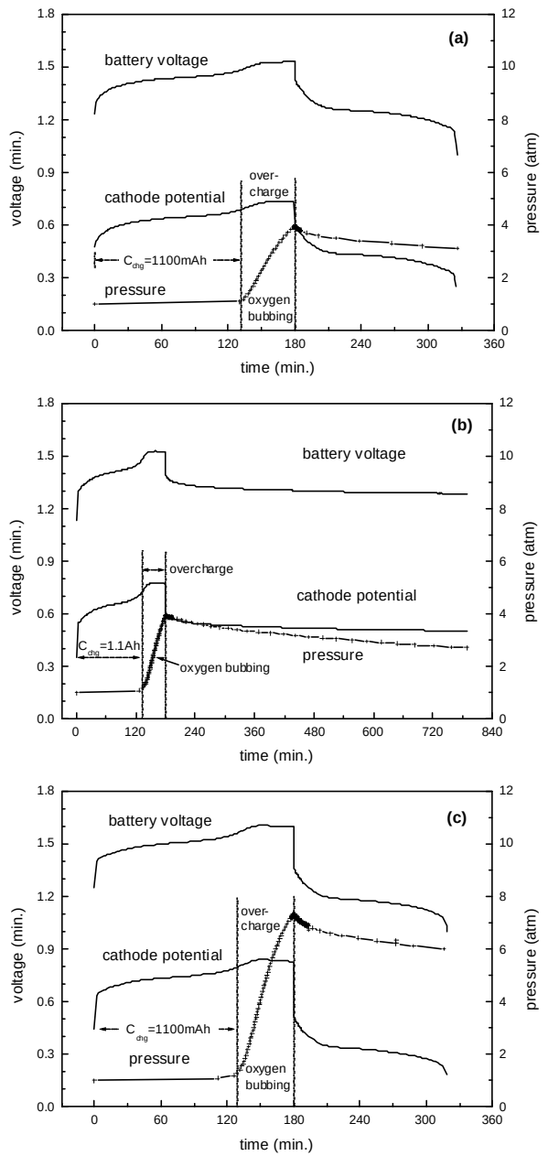

Fig. 1 Ni/MH battery voltage, cathode potential and internal gas pressure curves with different conditions: (a) and (b) electrodes half immerged in electrolyte; (c) electrodes fully immerged in electrolyte. Charge/discharge scheme: charge at 500mA for 3 hours, then (a) and (c) discharge at 500mA to 1.0V; (b) rest for 10 hours.

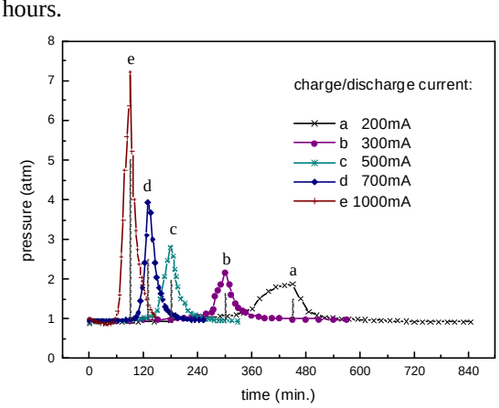

Fig. 2 Gas revolved and annihilated at different charge /discharge currents. Vertical dot lines fence out the charge/discharge stage for each curve.